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Part III



Technical Note N-921

CORROSION OF MATERIALS IN HYDROSPACE

PART III - TITANIUM AND TITANIUM ALLOYS

BY

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Internal Working Paper

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ABSTRACT

A total of 475 specimens of 10 titanium alloys were exposed at two different depths in the Pacific Ocean for six different periods of time varying from 123 to 1064 days to determine the effects of deep ocean environments on their corrosion resistance. Specimens of the alloys were also exposed in surface seawater for 181 days for comparison purposes.

Corrosion rates, types of corrosion, pit depths, effects of welding, stress corrosion cracking resistance and changes in mechanical properties are presented.

The alloys were immune to corrosion and stress corrosion cracking except alloy 13V-11Cr-3Al with unrelieved circular welds. This alloy with unrelieved circular welds failed by stress corrosion cracking after 181 days of exposure at the surface, 403 days at 6,780 feet and 402 days at 2,370 feet. The 13V-11Cr-3Al alloy with unrelieved butt welds failed by stress corrosion cracking when stressed at 75 percent of its yield strength after 35, 77 and 105 days of exposure at the surface.

The mechanical properties of the alloys were not affected.

Some information from TOTO in the Atlantic Ocean is included for comparative purposes.

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PREFACE

The U. S. Naval Civil Engineering Laboratory is conducting a research program to determine the effects of deep ocean environments on materials. It is expected that this research will establish the best materials to be used in deep ocean construction.

A Submersible Test Unit (STU) was designed, on which many test specimens can be mounted. The STU can be lowered to the ocean floor and left for long periods of exposure.

Thus far, two deep-ocean test sites in the Pacific Ocean have been selected. Six STUs have been exposed and recovered. Test Site I (nominal depth of 6,000 feet) is approximately 81 nautical miles west-southwest of Port Hueneme, California, latitude $33^{\circ}44'N$ and longitude $120^{\circ}45'W$. Test Site II (nominal depth of 2,500 feet) is 75 nautical miles west of Port Hueneme, California, latitude $34^{\circ}06'N$ and longitude $120^{\circ}42'W$. A surface sea water exposure site (V) was established at Point Mugu, California ($34^{\circ}06'N - 119^{\circ}07'W$) to obtain surface immersion data for comparison purposes.

This report presents the results of the evaluations of titanium and titanium alloys exposed at the above three test sites. Also, some information from TOTO is included for comparative purposes.



INTRODUCTION

The development of deep diving submarines which can stay submerged for long periods of time has focused attention on the deep ocean as an operating environment. This has created a need for information concerning the behavior of common materials of construction as well as newly developed materials with promising potentials, at depths in the ocean.

To study the problems of construction in the deep ocean, project "Deep Ocean Studies" was established. Fundamental to the design, construction and operation of structures, and their related facilities is information with regard to the deterioration of materials in deep ocean environments. This report is devoted to the portion of the project concerned with determining the effects of these environments on the corrosion of metals and alloys.

The test sites for the deep ocean exposures are shown in Figure 1 and their specific geographical locations are given in Table 1. The complete oceanographic data at these sites, obtained from NCEL cruises between 1961 and 1967, are summarized in Figure 2. Initially, it was decided to utilize the site at the 6,000 foot depth. Because of the minimum oxygen concentration zone found between the 2,000 and 3,000 foot depths, during the early oceanographic cruises, it was decided to establish a second exposure site (STU II-1 and II-2) at a nominal depth of 2,500 feet. For comparative purposes, the surface water site V was included.

A summary of the characteristics of the bottom waters 10 feet above the bottom sediments at the two deep ocean exposure sites and at the surface exposure site is given in Table 1.

Sources of information pertaining to the biological characteristics of the bottom sediments, biological deterioration of materials, detailed oceanographic data, and construction, emplacement and retrieval of STU structures are given in Reference 1.

The procedures for the preparation of the specimens for exposure and for evaluating them after exposure are described in Reference 2.

Previous reports pertaining to the performance of materials in the deep ocean environments are given in References 1 through 7.

This report is a discussion of the results obtained of the corrosion of titanium and titanium alloys for the six exposure periods shown in Table 1 and for 181 days of exposure five feet below the surface.

RESULTS AND DISCUSSION

The results presented and discussed herein also include the corrosion data for titanium exposed on the STU structures for the International Nickel Company, Incorporated as granted by Reference 8. Results from other participants in the NCEL exposures are also included; U. S. Navy Marine Engineering Laboratory (Reference 9), the Chemistry Division, NCEL (Reference 10), and U. S. Naval Air Engineering Center (Reference 11). Deep ocean data from the Atlantic Ocean (TOTO) are also included for purposes of comparison; Naval Research Laboratory (Reference 12) and Naval Applied Science Laboratory (Reference 13).

The chemical compositions of the titanium alloys are given in Table 2, their corrosion rates in Table 3, their stress corrosion behavior in Table 4 and the effect of corrosion on their mechanical properties in Table 5.

Corrosion

There was no corrosion of any of the alloys at the surface or at either nominal depth (2,500 or 6,000 feet) for any period of exposure except two alloys; the Navy Marine Engineering Laboratory reported a corrosion rate of 0.19 MPY for unalloyed titanium and of 0.18 MPY for the 6 Al-4V alloy after 123 days of exposure at a depth of 5,640 feet in the Pacific Ocean, Reference 9. They also reported no visible corrosion. For practical purposes, these values are considered to be inconsequential.

Alloys 75A, Ti-0.15 Pd, 5Al-2.5Sn, 6Al-4V and 13V-11Cr-3Al were fusion welded by the inert-gas shielded arc, non-consumable (tungsten-arc) electrode process (TIG). There were transverse butt welds and 3-inch diameter circular welds in the 6 inch by 12 inch specimens. The welding stresses of these specimens were not relieved by an annealing treatment in order to simulate a welded component not adaptable to stress relieving after welding. There was no visible corrosion of these welded alloys except for stress corrosion cracking of the 13V-11Cr-3Al alloy with the circular welds. This will be discuss under stress corrosion.

The 6Al-4V alloy was also exposed as:

- a. Wire, 0.020, 0.045 and 0.063 inch diameter
- b. Cables, 1/16"- 1 x 19, $\frac{1}{4}$ " - 6 x 19, $\frac{1}{2}$ " - 6 x 19 with Type 304 stainless steel swaged ends and $\frac{1}{2}$ " - 6 x 19 tied with mild steel wire.

- c. Flash welded tube.
- d. Flash welded sphere.
- e. Piece from a broken sphere.

There was no visible corrosion on any of the above specimens except for the Type 304 swaged fittings and the mild steel wire. The faying surfaces of the Type 304 swaged fittings were severely attacked by crevice corrosion. The mild steel wire used to tie the end of one titanium cable was corroded almost through by galvanic corrosion; the mild steel wire being anodic to the titanium cable.

The Naval Research Laboratory, Reference 12, and the Naval Applied Science Laboratory, Reference 13, reported no corrosion of titanium alloys, both unwelded and welded, at depths of 4,250 and 5,600 feet in the Tongue-of-the-Ocean, Atlantic Ocean after exposures varying from 102 to 1050 days.

Stress Corrosion

Specimens of the alloys stressed in various ways and to values equivalent to 35, 50 and 75 percent of their respective yield strengths were exposed at the surface for 180 days and at nominal depths of 2,500 and 6,000 feet for different periods of time.

The majority of the specimens were deformed by bowing to obtain the desired tensile stress in the central 2 inch length of the outer surface of the specimen as described in Reference 2. Many of these specimens, butt welded by the TIG process, were positioned such that the transverse weld bead was at the apex of the bow in the 2-inch length. Other specimens, 6" x 12", had a 3" diameter circular weld bead placed in the center as shown in Figure 3. The stresses induced by the welding operation were not relieved in order to retain the maximum residual stresses in the specimens. Still other specimens were in the shape of welded rings 9-5/8 inches outside diameter which were deformed different amounts in order to induce tensile stresses in the periphery at the ends of the restraining rods as shown in Figure 4.

The results of the stress corrosion tests are given in Table 4. There were no stress corrosion cracking failures of any of the alloys, both unwelded and butt welded, stressed at values equivalent to as high as 75 percent of their respective yield strengths for 180 days of exposure at the surface, 402 days at the 2,370 foot depth and 751 days at the 5,640 foot depth, except for the butt welded 13V-11Cr-3Al alloy. The unrelieved butt welded 13V-11Cr-3Al alloy

failed by stress corrosion cracking when stressed at values equivalent to 75 percent (94,500 psi) of its yield strength after 35, 77 and 105 days of exposure at the surface in the Pacific Ocean. The stress corrosion cracks occurred at the edge of the weld bead as shown in Figure 5.

Metallographic examinations of unetched and etched sections in a plane parallel to the surface of the specimen showed that a secondary crack which started at the edge of the specimen in the parent metal away from and parallel to the main fracture was irregular and branching in nature as well as transgranular as shown in Figure 6. This is typical of the main fracture.

The Naval Applied Science Laboratory, Reference 10, reported no stress corrosion cracking of unwelded and butt welded 7Al-2Cb-1Ta alloy stressed at 100 percent of its yield strength after 199 days of exposure at a depth of 4,250 feet in the Tongue-of-the-Ocean, Atlantic Ocean.

The 6Al-4V alloy rings stressed as high as 60,000 psi (approximately 50 percent of its yield strength) (Figure 4) did not fail by stress corrosion cracking during 402 days of exposure at a depth of 2,370 feet.

Alloys 75A, Ti-0.15Pd, 5Al-2.5Sn, 7Al-2Cb-1Ta, 6Al-4V and 13V-11Cr-3Al were exposed with an unrelieved 3-inch diameter circular weld bead in the center of 6" x 12" specimens as shown in Figure 3. Only the 13V-11Cr-3Al alloy failed by stress corrosion cracking because of the residual welding stresses. Cracking occurred during surface exposure of 181 days, during 403 days of exposure at a depth of 6,780 feet, during 751 days of exposure at a depth of 5,640 feet, and during 402 days of exposure at a depth of 2,370 feet. The cracks in all cases were radial across the weld beads, a typical crack is shown in Figure 7. The crack in this case changed direction by 90 degrees (left side of Figure) just outside the weld bead because of the redistribution of the residual stresses.

Metallographic examination of a polished section of the crack taken in the plane of the sheet where it changed direction showed that the path of the crack was irregular and branching in nature as shown in Figure 8. After etching and reexamination it was found that the crack was predominantly transgranular as shown in Figure 9.

Mechanical Properties

The effect of exposure in sea water at nominal depths of 2,500 and 6,000 feet on the mechanical properties of the alloys is given in Table 5. These data show that the mechanical properties of the alloys were not adversely affected by exposure in sea water at nominal depths of 2,500 and 6,000 feet for periods of time as long as 751 days.

SUMMARY AND CONCLUSIONS

The purpose of this investigation was to determine the effects of deep ocean environments on the corrosion and stress corrosion of titanium alloys. To accomplish this, 473 specimens of 10 alloys were exposed at the surface for 181 days and at nominal depths of 2,500 and 6,000 feet for periods of time varying from 123 to 1064 days.

There was no visible corrosion nor any significant weight losses of any of the alloys after 181 days of exposure at the surface, 197 and 402 days at a nominal depth of 2,500 feet, and 123, 403, 751, and 1064 days at a nominal depth of 6,000 feet either in the sea water or the bottom sediment.

Alloys, unwelded and with transverse butt welds, were not susceptible to stress corrosion cracking when stressed at values equivalent to 75 percent of their respective yield strengths after 180 days of exposure at the surface, 402 days at a nominal depth of 2,500 feet, and 751 days of exposure at a nominal depth of 6,000 feet, except the butt welded 13V-11Cr-3Al alloy. This alloy failed by stress corrosion cracking after 35, 77 and 105 days of exposure at the surface. Flash welded rings of 6Al-4V alloy did not stress corrosion crack when stressed to 60,000 psi and exposed at a depth of 2,370 feet for 402 days. The residual stresses induced in 13V-11Cr-3Al alloy sheet by a 3-inch diameter unrelieved weld were great enough to cause stress corrosion cracking after 181 days of exposure at the surface, 403 days at 6,780 feet, and 402 days at 2,370 feet. The other alloys, 75A, Ti-0.15Pd, 5Al-2.5Sn, 7Al-2Cb-1Ta, and 6Al-4V, similarly welded were not susceptible to stress corrosion cracking either at the surface or at depth.

The mechanical properties of the alloys were not adversely affected by exposure in sea water at depth.

Differences in temperature, oxygen concentration, pressure and velocity of flow between the surface and depths in the Pacific Ocean appear to have no influence on the corrosion behavior of titanium alloys.

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Table 1. STU Locations and Bottom Water Characteristics

Site No.	Lat. N	Longit. W	Depth, ft	Exposure, Days	Temp., °C	Oxygen, ml/l	Salinity, ppt	pH	Current, Knots, Av.
Surface	-	-	65	-	11-17	5.4-6.5	33.76	7.9-8.3	Variable
I-1	33°44'	120°37'	5300	1064	2.6	1.2	34.51	7.5	0.03
I-2	33°44'	120°45'	5640	751	2.3	1.3	34.51	7.6	0.03
I-3	33°44'	120°45'	5640	123	2.3	1.3	34.51	7.6	0.03
I-4	33°46'	120°46'	6780	403	2.2	1.6	34.40	7.7	0.03
II-1	34°06'	120°42'	2340	197	5.0	0.4	34.36	7.5	0.06
II-2	34°06'	120°42'	2370	402	5.0	0.4	34.36	7.5	0.06
V	34°06'	119°07'	5	181	12-19	3.9-6.6	33.51	8.1	Variable

Table 2. Chemical Composition of Titanium Alloys, Percent by Weight

Alloy	C	Fe	N	H	O	Al	V	Cr	Other	Ti ₂ /	Source ^{3/}
Titanium	<0.1	-	0.02	-	-	-	-	-	-	INCO-8/ NCEL	
75A	0.027	0.20	0.026	0.004	-	-	-	-	-	Rem. Rem.	
75A	0.025	0.13	0.016	0.003	0.28	-	-	-	-	Rem.	
75A	0.025	0.14	0.017	0.003	0.32	-	-	-	-	Rem.	
Ti-0.15Pd	0.022	0.06	0.009	0.003	0.15	-	-	-	0.14Pd 0.15Pd	Rem. Rem.	
Ti-0.15Pd	0.022	0.05	0.012	0.004	-	-	-	-	-	Rem.	
Alpha Alloys											
5Al-2-1Sn	0.025	0.34	0.014	0.011	-	5.1	-	-	2.2Sn 2.4Sn 2.5Sn 1.0Ta 2.0Cb	Rem. Rem. Rem. Rem.	
5Al-2-5Sn	0.022	0.27	0.013	0.006	0.18	5.1	-	-	-	NCEL NCEL NCEL NCEL	
5Al-2-5Sn	0.025	0.35	0.013	0.008	0.17	5.1	-	-	-	Rem.	
7Al-2Cb-1Ta	0.023	0.06	0.006	0.002	0.07	7.0	-	-	-		
Alpha/Beta Alloys											
8Mn ^{1/}	0.20	-	0.07	0.15	-	-	-	-	8.0Mn 1.9Mo 3.0Mo 3.7Mo	Rem. Rem. Rem. Rem.	
14Al	-	1.9	-	-	<0.1	<0.1	2.1	-	-	NCEL 10/ NCEL	
4Al-3Mo-1V ^{1/}	0.08	0.25	0.05	0.15	-	4.25	1.0	-	-		
4Al-3Mo-1V	-	0.1	-	-	-	4.5	0.9	0.2	-	NCEL 10/ NCEL	
6Al-4V	0.023	0.15	0.015	0.007	-	6.0	3.9	-	-	Rem. Rem.	
6Al-4V	0.025	0.13	0.015	0.007	-	5.9	4.0	-	-	Rem. Rem.	
6Al-4V	0.022	0.08	0.013	0.007	0.11	5.8	4.0	-	-		
6Al-4V	-	<0.1	-	-	-	7.2	5.2	<0.1	-		
Beta Alloys											
13V-11Cr-3Al	0.027	0.17	0.027	0.008	-	3.1	13.4	11.4	-	Rem. Rem.	
13V-11Cr-3Al	0.021	0.14	0.027	0.010	0.12	3.0	13.6	10.9	-	NCEL NCEL	

^{1/} Nominal compositions^{2/} Rem. = Remainder^{3/} Numbers indicate references at end of paper.

Table 3. Corrosion Rates of Titanium Alloys

Alloy	Environment	Exposure, Days	Depth, Feet	Corrosion Rate ² /MPY ³	Type of Corrosion	Source
Titanium	W	123	5640	<0.1	No visible corrosion	INCO 8/
Titanium	S	123	5640	<0.1	No visible corrosion	INCO 8/
Titanium	W	403	6780	<0.1	No visible corrosion	INCO 8/
Titanium	S	403	6780	<0.1	No visible corrosion	INCO 8/
Titanium	W	751	5640	<0.1	No visible corrosion	INCO 8/
Titanium	S	751	5640	<0.1	No visible corrosion	INCO 8/
Titanium	W	1064	5300	<0.1	No visible corrosion	INCO 8/
Titanium	S	1064	5300	<0.1	No visible corrosion	INCO 8/
Titanium	W	197	2340	<0.1	No visible corrosion	INCO 8/
Titanium	S	197	2340	<0.1	No visible corrosion	INCO 8/
Titanium	W	402	2370	<0.1	No visible corrosion	INCO 8/
Titanium	S	402	2370	<0.1	No visible corrosion	INCO 8/
Titanium	W	123	5640	0.19	No visible corrosion	MEL 9/
Titanium	W	751	5640	<0.1	No visible corrosion	MEL 9/
Titanium	W	111	5600	0.0	No visible corrosion	NRL 12/
Titanium	W	1050	5600	0.0	No visible corrosion	NRL 12/
RC55	W	102	4250	<0.1	No visible corrosion	NASL 13/
RC55	W	199	4250	<0.1	No visible corrosion	NASL 13/
RC55	W	90	4500	<0.1	No visible corrosion	NASL 13/
RC55	W	180	4500	<0.1	No visible corrosion	NASL 13/
75A	W	123	5640	0.0	No visible corrosion	NCEL
75A	S	123	5640	0.0	No visible corrosion	NCEL
75A	W	403	6780	0.0	No visible corrosion	NCEL
75A	S	403	6780	0.0	No visible corrosion	NCEL
75A	W	751	5640	0.0	No visible corrosion	NCEL
75A	W	197	2340	0.0	No visible corrosion	NCEL
75A	S	197	2340	0.0	No visible corrosion	NCEL

Table 3. Continued

Alloy	Environment ³	Exposure, Days	Depth, Feet	Corrosion Rate ² /MPY	Type of Corrosion	Source ³
75A	W	402	2370	0.0	No visible corrosion	NCEL
75A	S	402	2370	0.0	No visible corrosion	NCEL
75A	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
75A ⁴ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
75A ⁵ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
Ti-0.15Pd ⁴ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
Ti-0.15Pd ⁵ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
5Al-2.5Sn ⁴ /	W	123	5640	<0.1	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	123	5640	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	S	123	5640	<0.1	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	S	123	5640	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	403	6780	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	W	403	6780	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	S	403	6780	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	S	403	6780	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	751	5640	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	751	5640	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	W	197	2340	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	197	2340	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	S	197	2340	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	S	197	2340	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	S	197	2340	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	W	402	2370	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	402	2370	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁵ /	S	402	2370	0.0	No visible corrosion	NCEL
5Al-2.5Sn ⁴ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
5Al-2.5Sn ⁵ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL

Table 3. - Continued

Alloy	Environment	Exposure, Days	Depth, Feet	Corrosion Rate ^g /MPY ²	Type of Corrosion	Source ³ /
7Al-12Zr	W	123	5640	0.0	No visible corrosion	NAEC ¹¹ /
7Al-2Cb-1Ta ⁴ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
7Al-2Cb-1Ta ⁵ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
8Mn	W	402	2370	0.0	No visible corrosion	NCEL
8Mn	S	402	2370	0.0	No visible corrosion	NCEL
140A	W	1064	5300	0.0	No visible corrosion	NCEL ¹⁰ /
4Al-3Mo-1V	W	123	5640	0.0	Slight amount of chemical attack with small amount of white corrosion products under similar metal couple.	NAEC ¹¹ /
4Al-3Mo-1V	W	1064	5300	0.0	No visible corrosion	NCEL
4Al-3Mo-1V	W	402	2370	0.0	No visible corrosion	NCEL
4Al-3Mo-1V	S	402	2370	0.0	No visible corrosion	NCEL
6Al-4V	W	123	5640	<0.1	No visible corrosion	NAEC ¹¹ /
6Al-4V	W	123	5640	0.18	No visible corrosion	MEL ⁷ /
6Al-4V	W	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₄ /	S	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₅ /	W	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₄ /	W	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₅ /	S	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₄ /	S	123	5640	0.0	No visible corrosion	NCEL
6Al-4V ₅ /	W	123	6780	0.0	No visible corrosion	NCEL
6Al-4V	W	403	6780	0.0	No visible corrosion	NCEL
6Al-4V ₄ /	S	403	6780	0.0	No visible corrosion	NCEL
6Al-4V ₅ /	W	403	6780	0.0	No visible corrosion	NCEL

Table 3. Continued

Alloy	Environment ⁷	Exposure, Days	Depth, Feet	Corrosion Rate ⁸ , MPY ² /	Type of Corrosion	Source ³ /
6Al-4V ⁴ /	W	403	6780	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	S	403	6780	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	S	403	6780	0.0	No visible corrosion	MEL ⁹ /
6Al-4V	W	751	5640	<0.1	No visible corrosion	NCEL
6Al-4V ⁴ /	W	751	5640	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	W	751	5640	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	W	751	5640	0.0	No visible corrosion	NCEL ¹⁰ /
6Al-4V	W	1064	5300	0.0	No visible corrosion	NCEL
6Al-4V	W	197	2340	0.0	No visible corrosion	NCEL
6Al-4V	S	197	2340	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	W	197	2340	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	W	197	2340	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	W	197	2340	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	S	197	2340	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	S	197	2340	0.0	No visible corrosion	NCEL
6Al-4V	W	402	2370	0.0	No visible corrosion	NCEL
6Al-4V	S	402	2370	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	W	402	2370	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	W	402	2370	0.0	No visible corrosion	NCEL
6Al-4V ⁴ /	S	402	2370	0.0	No visible corrosion	NCEL
6Al-4V ⁵ /	S	402	2370	0.0	No visible corrosion	NCEL
6Al-4V	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
6Al-4V ⁴ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
6Al-4V ⁵ /	W	181	5	0.0	No visible corrosion, fouling stains	NCEL
13V-11Cr-3Al ⁴ /	W	123	5640	<0.1	No visible corrosion	MEL ⁹ /
13V-11Cr-3Al ⁵ /	W	123	5640	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ⁴ /	W	123	5640	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ⁵ /	S	123	5640	<0.1	No visible corrosion	NCEL
13V-11Cr-3Al ⁵ /	S	123	5640	0.0	No visible corrosion	NCEL

Table 3. Continued

Alloy	Environment ^{3/}	Exposure, Days	Depth, Feet	Corrosion Rate ^{2/} MPY _±	Type of Corrosion	Source ^{3/}
13V-11Cr-3Al ^{4/}	W	403	6780	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{5/}	W	403	6780	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	S	403	6780	0.0	Stress corrosion cracks, radial, across weld bead	NCEL
13V-11Cr-3Al ^{5/}	S	403	6780	0.0	No visible corrosion	NCEL ^{4/}
13V-11Cr-3Al ^{4/}	W	751	5640	<0.1	No visible corrosion	MEL ^{5/}
13V-11Cr-3Al ^{5/}	W	751	5640	0.0	Stress corrosion cracks, radial, across weld bead	NCEL
13V-11Cr-3Al ^{5/}	W	751	5640	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	W	197	2340	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{5/}	W	197	2340	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	S	197	2340	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{5/}	S	197	2340	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	W	402	2370	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{5/}	W	402	2370	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	S	402	2370	0.0	Stress corrosion cracks, radial, across weld bead	NCEL
13V-11Cr-3Al ^{5/}	S	402	2370	0.0	No visible corrosion	NCEL
13V-11Cr-3Al ^{4/}	W	181	5	0.0	Stress corrosion cracks, radial, across weld bead	NCEL
13V-11Cr-3Al ^{5/}	W	181	5	0.0	No visible corrosion, fouling stains	NCEL

1/ W = specimens exposed on sides of STU in sea water
 S = specimens exposed in base of STU, partially embedded in bottom sediment
 2/ MPY = mils penetration per year calculated from weight loss
 3/ Numbers refer to references at end of paper

4/ Circular weld 3 inches in diameter in center of specimen, unrelieved
 5/ Transverse butt weld across width of specimen, unrelieved

Table 4. Stress Corrosion of Titanium Alloys

Alloy	Stress, KSI	Percent of Yield Strength	Exposure, Days	Depth, Feet	Specimens	
					Exposed	Failed
75A	24.5	35	403	6780	2	0
75A	24.5	35	197	2340	3	0
75A	35.0	50	403	6780	2	0
75A	35.0	50	197	2340	3	0
75A	35.0	50	402	2370	3	0
75A	52.6	75	403	6780	2	0
75A	52.6	75	197	2340	3	0
75A ₁ /	52.6	75	402	2370	3	0
75A ₁ ¹ /	28.8	35	180	5	3	0
75A ₁ ¹ /	41.2	50	180	5	3	0
75A ₁ ¹ /	61.7	75	180	5	3	0
75A ₂ ² /	Welding stresses		181	5	4	0
Ti-0.15Pd ₁ ¹ /	23.8	35	180	5	3	0
Ti-0.15Pd ₁ ¹ /	33.9	50	180	5	3	0
Ti-0.15Pd ₁ ¹ /	50.8	75	180	5	3	0
Ti-0.15Pd ₂ ² /	Welding stresses		181	5	4	0
5Al-2.5Sn ₁ ¹ /	42.9	35	123	5640	3	0
5Al-2.5Sn ₁ ¹ /	42.9	35	403	6780	2	0
5Al-2.5Sn ₁ ¹ /	42.9	35	751	5640	3	0
5Al-2.5Sn ₁ ¹ /	42.9	35	197	2340	3	0
5Al-2.5Sn ₁ ¹ /	61.3	50	123	5640	3	0
5Al-2.5Sn ₁ ¹ /	61.3	50	403	6780	2	0
5Al-2.5Sn ₁ ¹ /	61.3	50	751	5640	3	0
5Al-2.5Sn ₁ ¹ /	61.3	50	197	2340	3	0
5Al-2.5Sn ₁ ¹ /	92.0	75	123	5640	3	0
5Al-2.5Sn ₁ ¹ /	92.0	75	403	6780	2	0 ³ /
5Al-2.5Sn ₁ ¹ /	92.0	75	751	5640	3	0 ³ /
5Al-2.5Sn ₁ ¹ /	92.0	75	197	2340	3	0
5Al-2.5Sn ₁ ¹ /	43.3	35	180	5	3	0
5Al-2.5Sn ₁ ¹ /	61.8	50	180	5	3	0
5Al-2.5Sn ₁ ¹ /	92.7	75	180	5	3	0
5Al-2.5Sn ₂ ² /	Welding stresses		123	5640	2	0
5Al-2.5Sn ₂ ² /	Welding stresses		403	6780	2	0 ⁴ /
5Al-2.5Sn ₂ ² /	Welding stresses		751	5640	2	0
5Al-2.5Sn ₂ ² /	Welding stresses		197	2340	2	0
5Al-2.5Sn ₂ ² /	Welding stresses		402	2370	2	0
5Al-2.5Sn ₂ ² /	Welding stresses		181	5	4	0

Table 4. Continued

Alloy	Stress, KSI	Percent of Yield Strength	Exposure, Days	Depth, Feet	Specimens	
					Exposed	Failed
7Al-2Cb-1Ta ^{10/}	110	100	102	4250	1	0
7Al-2Cb-1Ta ^{10/}	110	100	102	4250	1	0
transverse weld						
7Al-2Cb-1Ta ^{10/}	110	100	102	4250	1	0
longitudinal weld						
7Al-2Cb-1Ta ^{10/}	110	100	199	4250	1	0
7Al-2Cb-1Ta ^{10/}	110	100	199	4250	1	0
transverse weld						
7Al-2Cb-1Ta ^{10/}	110	100	199	4250	1	0
longitudinal weld						
7Al-2Cb-1Ta ^{1/}	34.9	35	180	5	3	0
7Al-2Cb-1Ta ^{1/}	49.9	50	180	5	3	0
7Al-2Cb-1Ta ^{1/}	74.9	75	180	5	3	0
7Al-2Cb-1Ta ^{2/}	Welding stresses		181	5	4	0
6Al-4V ^{1/}	47.6	35	123	5640	3	0
6Al-4V ^{1/}	48.8	35	123	5640	3	0
6Al-4V ^{1/}	47.6	35	403	6780	2	0
6Al-4V ^{1/}	48.8	35	403	6780	2	0
6Al-4V ^{1/}	47.6	35	751	5640	3	0
6Al-4V ^{1/}	48.8	35	751	5640	3	0
6Al-4V ^{1/}	47.6	35	197	2340	3	0
6Al-4V ^{1/}	48.8	35	197	2340	3	0
6Al-4V ^{1/}	68.0	50	123	5640	3	0
6Al-4V ^{1/}	69.7	50	123	5640	3	0
6Al-4V ^{1/}	68.0	50	403	6780	2	0
6Al-4V ^{1/}	69.7	50	403	6780	2	0
6Al-4V ^{1/}	68.0	50	751	5640	3	0
6Al-4V ^{1/}	69.7	50	751	5640	3	0
6Al-4V ^{1/}	68.0	50	197	2340	3	0
6Al-4V ^{1/}	69.7	50	197	2340	3	0
6Al-4V ^{1/}	68.0	50	402	2370	3	0
6Al-4V ^{1/}	102.0	75	123	5640	3	0
6Al-4V ^{1/}	104.5	75	123	5640	3	0
6Al-4V ^{1/}	102.0	75	403	6780	2	0
6Al-4V ^{1/}	104.5	75	403	6780	2	0
6Al-4V ^{1/}	102.0	75	751	5640	3	0
6Al-4V ^{1/}	104.5	75	751	5640	3	0
6Al-4V ^{1/}	102.0	75	197	2340	3	0
6Al-4V ^{1/}	104.5	75	197	2340	3	0
6Al-4V ^{1/}	102.0	75	402	2370	3	0
6Al-4V ^{1/}	46.1	35	180	5	3	0
6Al-4V ^{1/}	65.8	50	180	5	3	0
6Al-4V ^{1/}	98.7	75	180	5	3	0

Table 4. Continued

Alloy	Stress, KSI	Percent of Yield Strength	Exposure, Days	Depth, Feet	Specimens	
					Exposed	Failed
6Al-4V ² / ₂	Welding stresses		123	5640	2	0
6Al-4V ² / ₂	Welding stresses		403	6780	2	0
6Al-4V ² / ₂	Welding stresses		751	5640	2	0
6Al-4V ² / ₂	Welding stresses		197	2340	2	0
6Al-4V ² / ₂	Welding stresses		402	2370	2	0
6Al-4V ² / ₂	Welding stresses		181	5	4	0
13V-11Cr-3Al ¹ / ₁	48.8	35	123	5640	3	0
13V-11Cr-3Al ¹ / ₁	48.8	35	403	6780	2	0
13V-11Cr-3Al ¹ / ₁	48.8	35	751	5640	3	0
13V-11Cr-3Al ¹ / ₁	48.8	35	197	2340	3	0
13V-11Cr-3Al ¹ / ₁	69.8	50	123	5640	3	0
13V-11Cr-3Al ¹ / ₁	69.8	50	403	6780	2	0
13V-11Cr-3Al ¹ / ₁	69.8	50	751	5640	3	0
13V-11Cr-3Al ¹ / ₁	69.8	50	197	2340	3	0
13V-11Cr-3Al ¹ / ₁	104.6	75	123	5640	3	0
13V-11Cr-3Al ¹ / ₁	104.6	75	403	6780	2	0
13V-11Cr-3Al ¹ / ₁	104.6	75	751	5640	3	0
13V-11Cr-3Al ¹ / ₁	104.6	75	197	2340	3	0
13V-11Cr-3Al ¹ / ₁	44.2	35	180	5	3	0
13V-11Cr-3Al ¹ / ₁	63.0	50	180	5	3	0
13V-11Cr-3Al ¹ / ₁	94.5	75	180	5	3	3
13V-11Cr-3Al ² / ₂	Welding stresses		123	5640	2	0
13V-11Cr-3Al ² / ₂	Welding stresses		403	6780	2	1
13V-11Cr-3Al ² / ₂	Welding stresses		751	5640	2	1
13V-11Cr-3Al ² / ₂	Welding stresses		197	2340	2	0
13V-11Cr-3Al ² / ₂	Welding stresses		402	2370	2	1
13V-11Cr-3Al ² / ₂	Welding stresses		181	5	4	1

- 1/ Transverse butt weld, unrelieved, across specimen at apex of bow.
 2/ Circular weld 3 inches in diameter in center of specimen, unrelieved.
 3/ Two specimens lost when structure was turned on its side and dragged along the bottom.
 4/ One specimen lost when structure was turned on its side and dragged along the bottom.
 5/ Three specimens lost when structure was turned on its side and dragged along the bottom.
 6/ Specimens failed at edge of weld beads after 35, 77 and 105 days.
 7/ Specimen partially embedded in bottom sediment cracked radially across the weld bead.
 8/ Specimen in sea water cracked radially across the weld bead.
 9/ Three specimens lost during a storm.
 10/ Reference 13

Table 5. Percent Change in Mechanical Properties of Titanium Alloys Due to Corrosion

Alloy	Exposure		Original Properties			Tensile Strength, Percent	Tensile Strength	Yield Strength	Percent Change
	Depth, Feet	Days	Tensile Strength, KSI	Yield Strength, KSI	Elongation Percent				
75A	-	-	87.2	70.1	29.7	-	+3.6	+5.0	-
75A	5640	123	-	-	-	-	+4.0	+4.2	-4.7
75A	6780	403	-	-	-	-	+4.0	+11.0	-15.5
75A	5640	751	-	-	-	-	+4.5	+7.8	-14.8
75A	2340	197	-	-	-	-	+6.4	+7.1	-11.2
75A	2370	402	-	-	-	-	-	-	-13.2
5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} /	-	-	130.1	122.6	14.0	-	+10.0	+10.3	-
5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} /	6780	403	-	-	-	-	+3.5	+4.5	-13.2
5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} /	5640	751	-	-	-	-	+5.0	+4.2	-10.8
5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} / 5Al-2.5Sr _{1/2} /	2370	402	-	-	-	-	-	-	-15.0
8Mn	-	-	132.4	116.1	11.8	-	+2.4	+3.2	-
8Mn	2370	402	-	-	-	-	-	-	+33.1
4Al-3Mo-1V	-	-	201.4	180.4	4.0	-	-	-	-
4Al-3Mo-1V	2370	402	-	-	-	+1.2	-	-2.2	+18.8
6Al-4V	-	-	139.7	136.0	14.0	-	+15.6	+15.7	-
6Al-4V	6780	403	-	-	-	-	+0.2	+3.5	0.0
6Al-4V	5640	751	-	-	-	-	+2.3	+3.2	-7.3
6Al-4V	2340	197	-	-	-	-	+7.2	+6.0	+1.8
6Al-4V	2370	402	-	-	-	-	-	-	-0.7
6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} /	-	-	148.4	139.3	12.5	-	+4.0	-0.5	-
6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} /	6780	403	-	-	-	-	+3.1	+4.3	-12.8
6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} /	5640	751	-	-	-	-	+2.3	+1.2	-12.8
6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} / 6Al-4V _{1/2} /	2370	402	-	-	-	-	-	-	-8.4

Table 5. Continued

Alloy	Exposure		Original Properties			Tensile Strength	Percent Change Yield Strength	Elongation
	Depth, Feet	Days	Tensile Strength, KSI	Yield Strength, KSI	Elongation, Percent			
13V-11Cr-3Al ^{1/} ₁	-	-	143.9	139.5	8.5	-	-	-
13V-11Cr-3Al ^{1/} ₁	6780	403	-	-	-	+17.8	+18.1	-1.8
13V-11Cr-3Al ^{1/} ₁	5640	751	-	-	-	+17.8	+19.6	+5.9
13V-11Cr-3Al ^{1/} ₁	2370	402	-	-	-	+6.1	+5.1	-21.8

1/ Transverse butt weld across mid-point of reduced section of tensile specimens.

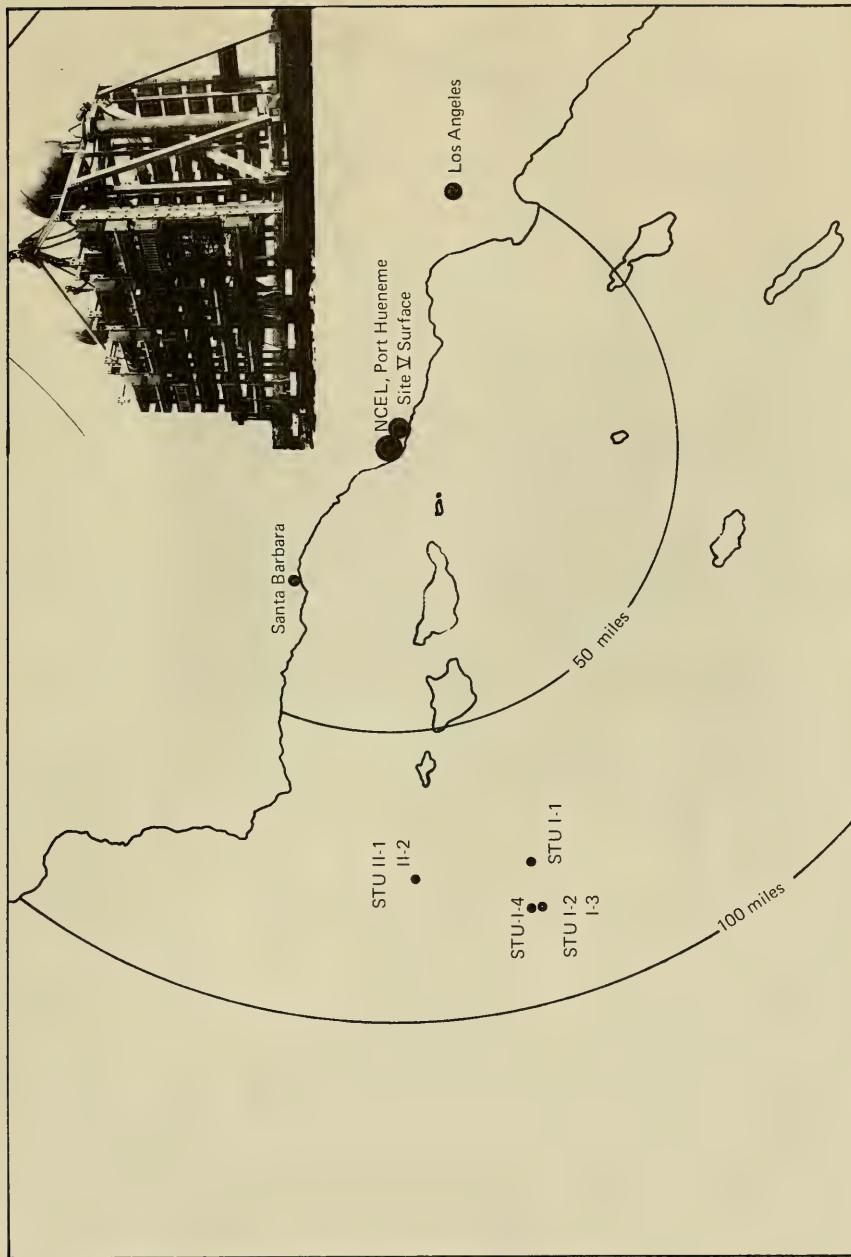


Figure 1. Area map showing STU sites off the Pacific Coast; STU structure in inset.

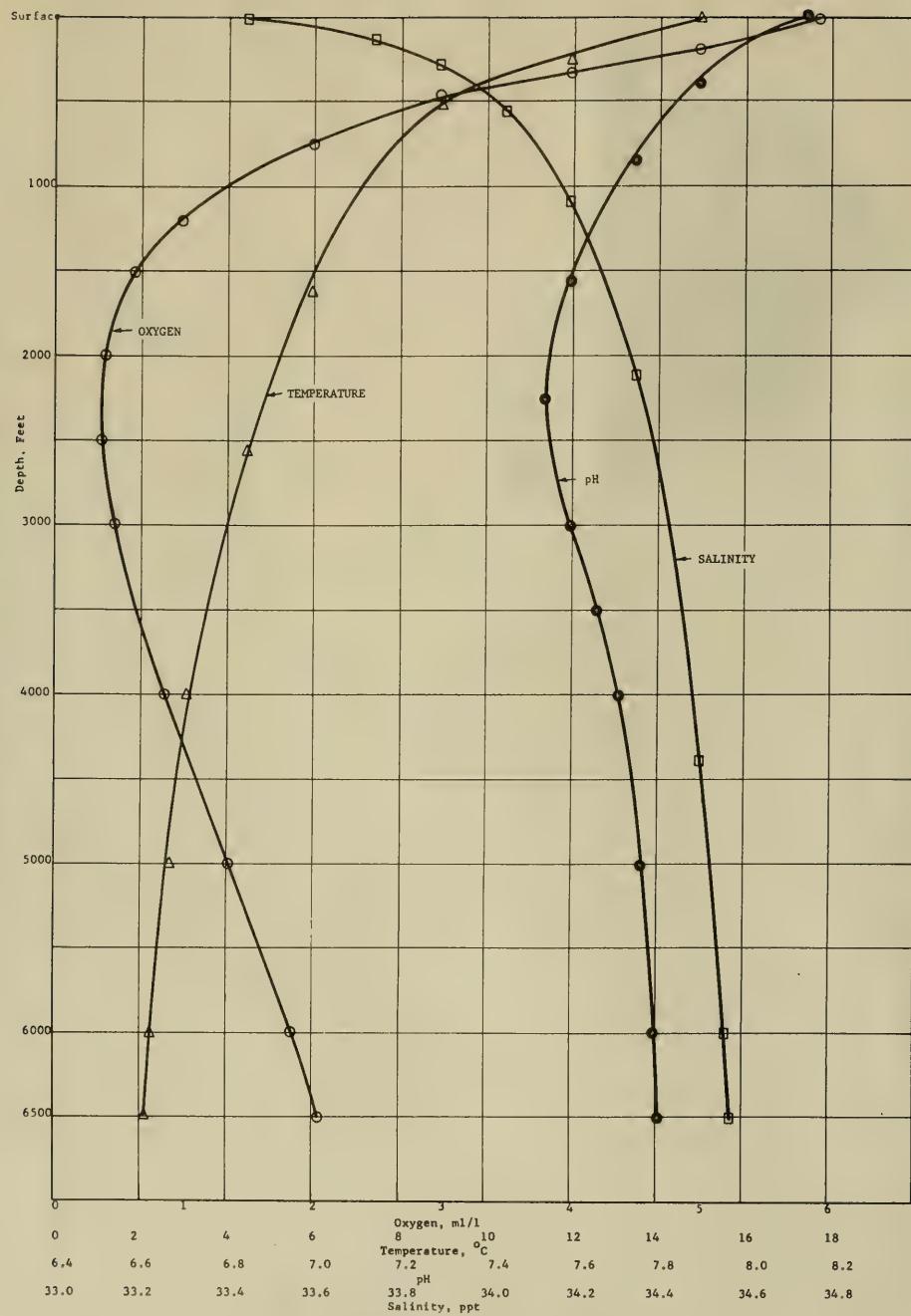


Figure 2. Oceanographic data at STU sites.



Figure 3. Circular weld (3" diameter) in 6" x 12" specimen,
unrelieved.

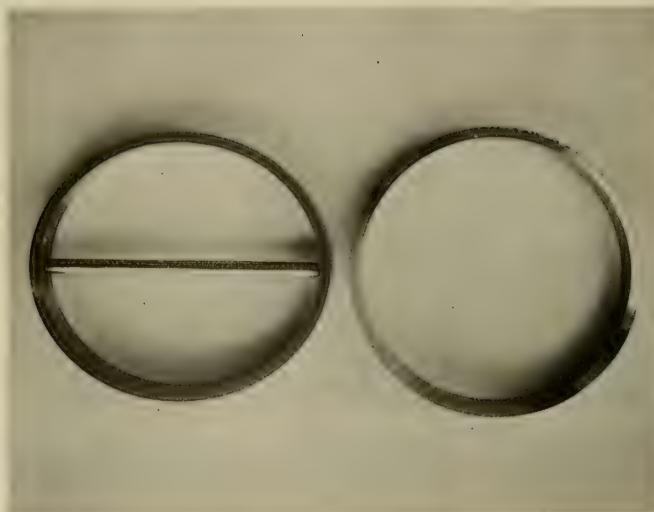


Figure 4. Alloy 6Al-4V welded rings deformed to induce stresses.

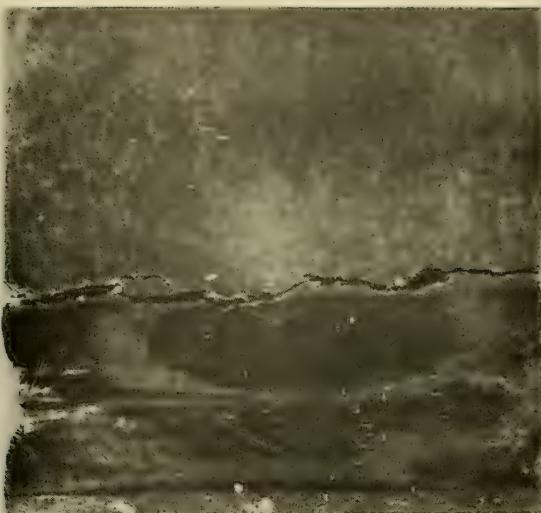


Figure 5. Stress corrosion crack across specimen of 13V-11Cr-3A1 alloy at the edge of the weld bead. Note secondary branching cracks extending from main fracture.



Figure 6. Secondary crack in parent metal away from and parallel to main fracture. Crack is branching in nature and transgranular. Etched in lactic, hydrofluoric and nitric acid mixture. X100.

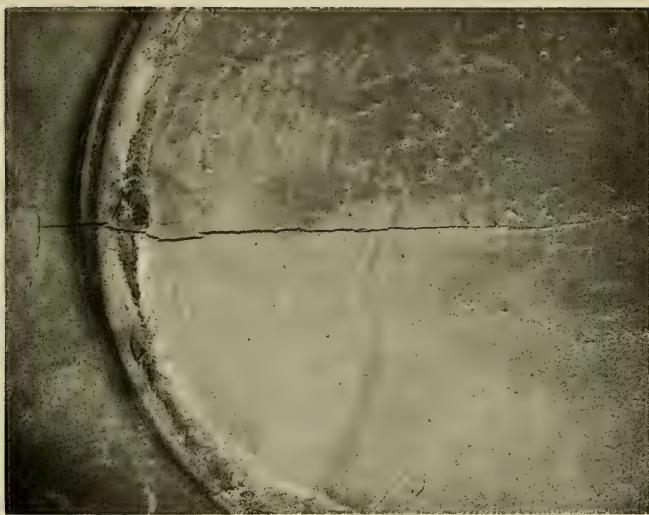


Figure 7. Radial stress corrosion crack across weld bead
of 13V-11Cr-3Al.



Figure 8. Irregular, branching stress corrosion crack in
13V-11Cr-3A1. Unetched. X100.

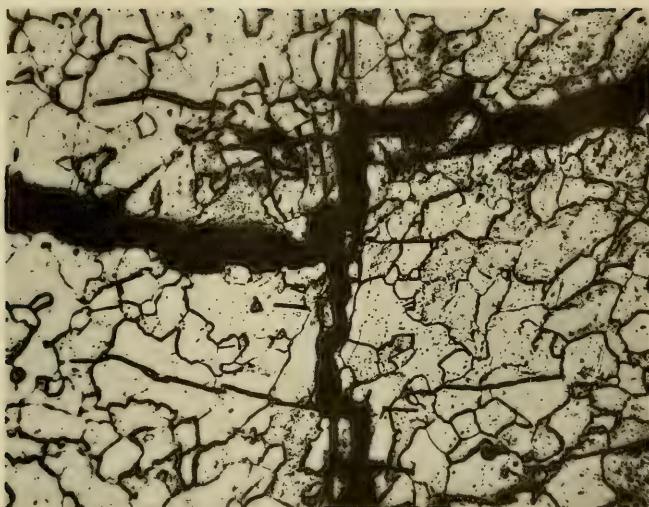


Figure 9. Same area as shown in Figure 6 etched to show that crack is predominantly transgranular. Etched in lactic- hydrofluoric-nitric acids. X100.



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13. ABSTRACT

A total of 475 specimens of 10 titanium alloys were exposed at two different depths in the Pacific Ocean for six different periods of time varying from 123 to 1064 days to determine the effects of deep ocean environments on their corrosion resistance. Specimens of the alloys were also exposed in surface seawater for 181 days for comparison purposes.

Corrosion rates, types of corrosion, pit depths, effects of welding, stress corrosion cracking resistance and changes in mechanical properties are presented.

The alloys were immune to corrosion and stress corrosion cracking except alloy 13V-11Cr-3Al. This alloy with unrelieved circular welds failed by stress corrosion cracking after 181 days of exposure at the surface, 403 days at 6,780 feet and 402 days at 2,370 feet. The 13V-11Cr-3Al alloy with unrelieved butt welds failed by stress corrosion cracking when stressed at 75 percent of its yield strength after 35, 77 and 105 days of exposure at the surface.

The mechanical properties of the alloys were not affected.

Some information from TOTO in the Atlantic Ocean is included for comparative purposes.

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